

Annual Progress Report for 1967 - 1968

to the

National Aeronautical and Space Administration

by

Lester H. Germer

"CHEMICAL REACTIONS AT METAL SURFACES"

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Principal Investigator: Lester H. Germer

Department of Applied Physics

Cornell University

Ithaca, New York 14850

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During the year from May 1, 1967 to April 30, 1968, the following people have worked on this project:

L. H. Germer	Principal Investigator
J. W. May	Postdoctoral Fellow
R. J. Szostak	Postdoctoral Fellow, on leave from Fritz-Haber Institute, Berlin, Germany. He returned to Germany in December 1967.
C. C. Chang	Graduate Student; received Ph.D. degree and is no longer here.
J. C. Tracy	Graduate Student

We have published during the year:

"Thermally Ordered Oxygen on a Nickel Surface",
L. H. Germer, J. W. May and R. J. Szostak, Surface
Science 7, 430-447 (1967).

"Oxidation of the (112) Face of Tungsten",
C. C. Chang and L. H. Germer, Surface Science
8, 115-129 (1967).

The reprints of each of these two papers were sent to NASA. We do not review them here.

We have now in press the following papers:

"Incipient Oxidation of (110) Nickel",
J. W. May and L. H. Germer, accepted for
publication in Surface Science.

Five copies of the manuscript of this paper were furnished to NASA in February 1968. Reprints will be sent as soon as available.

"Temperature Controller for LEED Experiments",
J. C. Tracy, submitted to Review of Scientific
Instruments, March 28, 1968.

Five copies of the manuscript of this paper are attached to this

report. It is not reviewed here.

We have completed the manuscript of a paper:

"Hydrogen and Oxygen on a (110) Nickel Surface",
J. W. May and L. H. Germer

This will be presented at the Fourth International Materials Symposium to be held at Berkeley, California June 17-21, 1968. It will be published in the book of the Conference. The work will be reviewed only briefly below. Five copies of the manuscript are attached.

The manuscript of another paper will be ready for publication in a few more weeks:

"Ammonia Adsorption and Decomposition on a Tungsten (211) Surface", J. W. May, R. J. Szostak and L. H. Germer.

This will be sent to the Journal of Chemical Physics or to Surface Science. Five copies of the manuscript will be sent to NASA as soon as available. This work is reviewed briefly below.

The following additional projects are under way:

"Work Function and Surface Structure Correlations in the Adsorption of Oxygen on Single Crystal Planes of Tungsten", J. C. Tracy and J. M. Blakely (J. M. Blakely is Associate Professor, working on LEED investigations but not supported by this contract).

This paper will be presented at the Fourth International Materials Symposium to be held at Berkeley, California June 17-21, 1968. This paper is reviewed very briefly below.

Additional research work by J. C. Tracy, not covered above, is also reviewed briefly below.

BRIEF REVIEWS OF ACCOMPLISHMENTS

The paper, "Incipient Oxidation of a (110) Nickel Surface", which is in press, represents, in the opinion of the Principal Investigator, a major contribution to the understanding of corrosion processes. It presents and establishes new and basic views about corrosion of potentially great importance. But, because copies of the manuscript are already in the hands of NASA, this work is not reviewed here.

"Hydrogen and Oxygen on a (110) Nickel Surface"

This paper is divided into three parts. In the first part, evidence is brought forward that the nickel atoms on this single crystal surface are rearranged at room temperature when the surface is exposed to hydrogen. This alters previous views about adsorption and, in the opinion of the Principal Investigator, is one of the most important results ever found in the study of surfaces. This conclusion has been promulgated before but the new evidence presented here is the most conclusive so far found. The second part of this paper describes the reaction at room temperature of oxygen with a surface previously covered by hydrogen. The stronger adsorption of oxygen is found to dominate the situation and most of the adsorption of oxygen takes place just as if the hydrogen were not present. In the third part of the paper is described the reaction of hydrogen with an oxygen covered surface. The efficiency of removal of oxygen varies between 10^{-5} at 400°K to the highest measured value of 0.02 at 800°K . At intermediate

temperatures the growth of islands of clean metal modifies greatly the course of the reaction. It leads to an understanding of the rather well known increase of rate of reduction of oxide with time. This was described in Langmuir in 1922 (and by others) but heretofore has not been understood.

"Catalytic Decomposition of Ammonia on a Single Crystal Tungsten Surface"

Ammonia is adsorbed upon a tungsten surface without decomposition. When a surface covered by ammonia is heated, hydrogen is evolved at 500°K leaving NH_2 radicals on the surface. These become well ordered at about 800°K into a rather simple structure in which the nitrogen atoms are bound to each other by hydrogen bonds in a single monolayer lying upon the surface. With heating above this temperature some hydrogen and nitrogen are evolved with continuous stretching of the hydrogen bonds and expansion of the structure in the $[110]$ surface direction. At an expansion of about 12 percent the bonds break and the NH_2 radicals are held independently to the surface with an arrangement which is not detectably influenced by the presence of attached hydrogen, i.e. the arrangement seems to be same as that of pure nitrogen. At 1200°K this NH_2 is vaporized from the surface in the form of N_2 and atomic hydrogen. This work represents, in the opinion of the Principal Investigator, a major advance in understanding catalytic processes.

"Work Function and Surface Structure Correlation in the Adsorption of Oxygen on Single Crystal Planes of Tungsten"

Work function changes have been measured by the Kelvin method. Work function has been found to increase on all tungsten

crystal planes with oxygen coverage. A minimum develops at about one monolayer coverage on the (112) plane, interpreted as depolarization between surface dipoles, but on other planes alteration is monotonically increasing.

Other Research of J. C. Tracy

The tungsten crystal planes (112) and (100) develop (110) facets when covered by oxygen and heated. Under the same conditions, the (111) planes develop first (112) facets and then (110) facets upon the already formed (112) facets. After oxygen and heat treatment all of these surfaces have the same work function, as one might expect from the fact that the final surface facets are crystallographically identical. This work, constituting the Tracy Ph.D. thesis, is nearly completed.

A Few Closing Comments

The Principal Investigator has published twenty-five (25) papers in this field since coming to Cornell in December 1961.

The LEED technique was originally developed by the Principal Investigator. Commercial equipment is being built now by at least a half dozen manufacturers in at least three different countries. These are being used in about 100 laboratories in at least 8 different countries. (U.S.A., England, Japan, France, Germany, Netherlands, Russia and Sweden.) Because of his beginning work in the field of this proposal, a very considerable fraction of the best work published up to this time has been carried out by the Principal Investigator. His position in the

field is still dominant.

The experimental procedures in his laboratory at Cornell University have not yet been so well developed in any other laboratory in the world. The equipment is in excellent operating condition. Its replacement value is greatly in excess of \$60,000.

Proposals

The work on ammonia decomposition has been planned and carried out by Dr. J. W. May and Dr. R. J. Szostak. Dr. May goes to the Bartol Research Foundation of the Franklin Institute on September 1, 1968. Up to this time he hopes to extend the work to cover a few features which are not yet clear. We have formulated plans for experiments on ammonia synthesis to be carried out during the coming year.

The Principal Investigator will also extend the investigation of oxidation to develop models of how individual oxygen and metal atoms move upon a surface under the driving force resulting from the energy of oxygen adsorption.

Lester H. Germer